



International Congress on Ultrasonics, Universidad de Santiago de Chile, January 2009

Ultrasonic Surface Modification of Electronics Materials

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Abstract

The electronics industry has always had a requirement for a range of metallised dielectric materials to form the conductive tracks used in many electronic products. It is essential that there is excellent adhesion between the dielectric material and the metal or other conductive track since without this failure of the device can occur. Surface modification of the substrate is one way to achieve good adhesion. Traditional wet chemical methods of surface modification employed in electronic manufacturing tend to be very cost effective but use hazardous, oxidizing, corrosive chemistry operate at elevated temperatures (high energy requirements) and require copious rinsing (high water usage). With the introduction of stricter health and safety and environmental legislation it is essential that 'greener' methods of surface modification are investigated. A study is currently being carried out evaluating sonochemical surface modification processes on a range of materials used in electronic manufacturing. This work has already shown that some materials can be surface modified using ultrasound through water. However, process times are still relatively long (30-60 minutes) and for the technique to become commercially viable they must be significantly reduced. One way to increase the ultrasonic intensity is to change the solvent and 'solvent swell' in a traditional surface modification process that can dramatically improve the adhesion of metal deposited on that material and a number of solvents have been screened. The efficacy of the whole process has been determined using methods such as scanning electron microscopy, contact angle measurements and the determination of adhesion of the plated metal.

Keywords : sonochemical, surface modification, electronics, materials

1. Introduction

In the electronics industry many different materials are required for plating purposes. Printed electronics have come a long way in recent times with the development of smaller printed circuit boards, radio frequency chips, and mobile internet devices such as laptops, mobile telephones and PDA's. Printing may now occur on many different types of materials such as plastics and polymers, glass and ceramics and even paper. Many metals are deposited or

printed onto substrate plastic materials, for example circuit boards used in computers and laptops. In order for a complete and durable finish the plastic material substrate used must be treated first in order to make it more amenable for a metal such as copper to be placed or plated onto it. One way to achieve this is to undergo surface modification of the substrate material prior to plating. In current treatment processes preparing a plastic surface for printing an electronic circuit onto it is fairly time consuming as it involves several steps. The process tends to involve 3 stages. The first stage is to dip the material into a solvent such as N-methylpyrrolidinone or butyl carbitol for a period of time from 5 to 15 minutes depending upon the material being treated. Once the dipping time is complete the sample must be rinsed at least twice to prevent carry over of the solvent into the next stage which can be something like dipping into a permanganate solution. This solution is often used to activate and remove material from the surface of the plastic. Once again a minimum of 5 to 15 min dipping in the bath is required. Two more rinse steps again are required to prevent carry over and the final step is a final neutralisation step with 2 more rinsing step again. The whole process can take up to one hour before plating even takes place.

Table 1 – Traditional swell and etch process

Chemistry	Time / min	Temp / °C
Solvent Swell	10	85
Rinse	5	
Rinse	5	
Etching phase	10	85
Rinse	5	
Rinse	5	
Neutralizer	3	RT-50
Rinse	3	
Rinse	1	

In addition to the long process times high temperatures and large amounts of water used there are often quite corrosive and carcinogenic chemicals involved in these processes such as hydrofluoric acid which is used to treat ceramics and glass and chromic acid is still used to treat materials such as ABS (acrylonitrile copolymer). Other solvents used can be highly flammable, or have high volatility and also incur their own environmental and health and safety issues which must all be considered.

The use of ultrasound is seen as a greener cleaner alternative to using high temperatures and corrosive chemicals. On sonication cavitation bubbles are formed within a liquid. Their subsequent growth within that medium and at the correct point in time, their subsequent collapse releases high temperatures and pressures within the medium. Of more interest to us is the manner of the collapse of the cavitation bubble. When a cavitation bubble collapses near to a solid surface, such as plastic material dipped into a solvent, the cavitation bubble exhibits asymmetrical collapse and a microjet of liquid is forced towards the solid surface. This microjet of liquid is able to impact the surface and cause surface modification alongside surface cleaning and mass transfer of materials to and from the substrate. Another point of interest is the possible chemical changes initiated within the liquid due to cavitation collapse. In the presence of water the formation of cavitation bubbles, and the high temperatures and pressures within them, can result in the formation of radicals such as OH and H[•] due to the sonochemical decomposition of water vapour within the cavitation bubble itself. On collapse of the bubble these radicals are thrown into the bulk liquid where they are able to attack the surface of any solid material within the solvent resulting in chemical reactions and breaking of bonds at the surface of the plastic substrate itself.

2. Experimental

All experiments were performed at 40 °C in deionised water using a 20kHz ultrasonic probe dipped into a beaker containing the solvent under study and substrate material. The system was cooled using a within a water jacket. The ultrasonic treatment process consisted of 4 steps

1. Sonication 40 °C, 4 - 60 minutes
 2. Cold water rinse, 5 minutes
 3. DI water rinse, 1 minute
 4. Dry
- Total process time – 10- 66 minutes

This was compared to the traditional swell and etch process described in Table 1 above.

Initial experiments were undertaken using an industry named product known as Isola 370 HR. Isola is an epoxy bonded laminate material which consists of glass fibers to strengthen it within an epoxy resin matrix. It has a dielectric constant of 3.92 and a Tg of 180 and as a result it is very hard/inflexible at room temp. Its dissipation factor is 0.0025 so the current signal is not attenuated through the substrate from the copper circuit. After treatment the material was evaluated using standard parameters of weight loss, contact angle, gloss meter readings, roughness and adhesion test, with adhesion levels being determined by how much material remains after the tape is removed and finally scanning electron microscopy (SEM) which provided an actual visual observation of the surface itself.

3. Results

3.1. Weight loss

The longer the sonication step the more weight loss was observed. However least 50% more mass was lost using the traditional method compared to the sonication process however this does not mean that more effective adhesion will be.

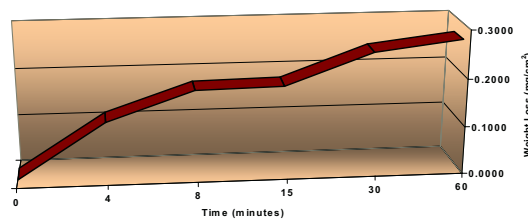


Fig.1 Weight Loss readings.

3.2. Contact angle

The traditional swell and etch process gave a final contact angle of 71.6. This was achieved within 30 minutes of sonication and the longer we sonicated the lower the contact angle suggesting surface activation.

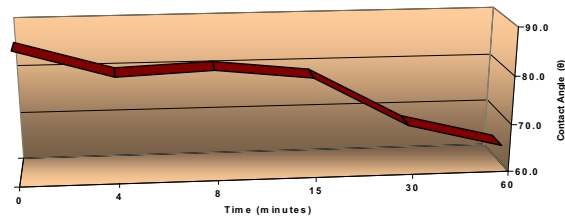


Fig.2 Contact Angle readings.

3.3. Gloss meter readings

All the values were very low and so these results must be treated with some caution however the traditional process gave a reading of 1.9% suggesting a smoother surface than that of the sonicated sample which very quickly reached 1.9% and continued to drop with a minimum reading of approx 1.1% reached within 30 minutes.

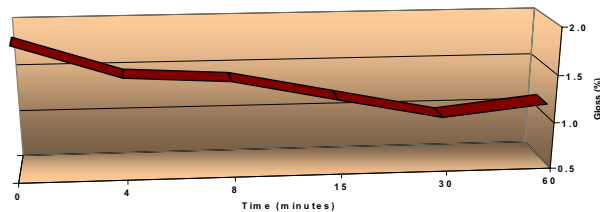


Fig.3 Gloss Meter readings.

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The roughness results were also very similar with maximum roughness achieved within 30 minutes and the traditional process giving lower readings suggesting a smoother surface with more disturbance/damage observed with the sonication.

3.4. Adhesion

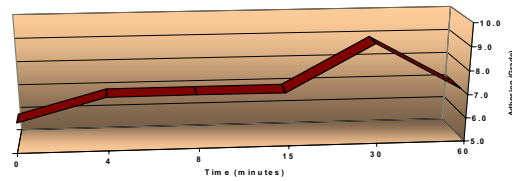
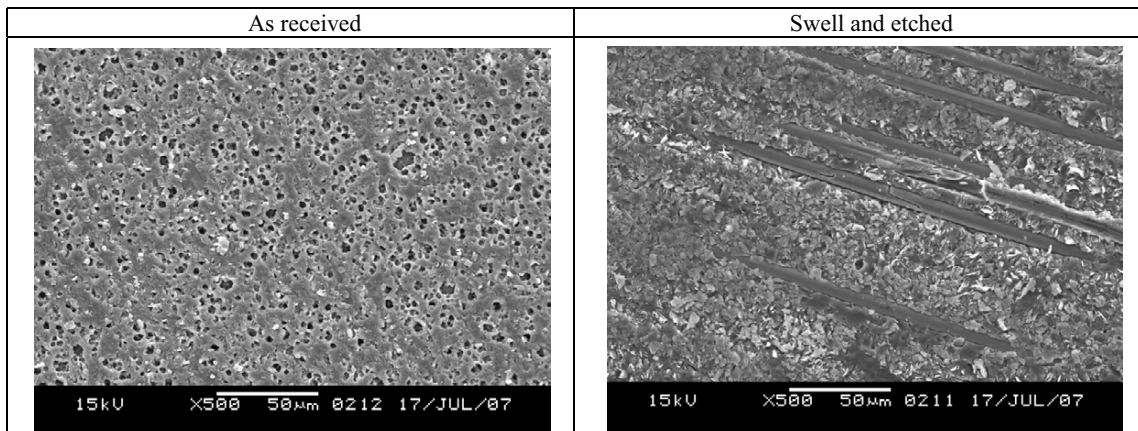


Fig.4 Adhesion Gradings

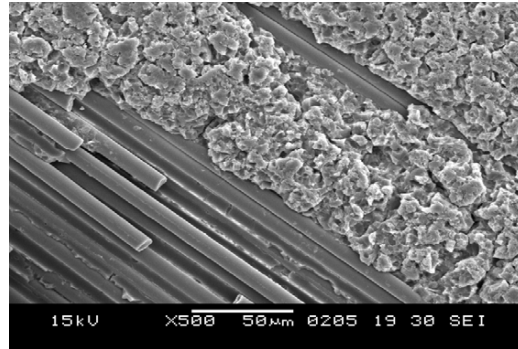
Finally the adhesion test gave us the greatest adhesion of electroless copper coating at 30 minutes sonication with the traditional process failing the tape test at this point.

3.5. Scanning Electron Microscopy

The most interesting results however were observed with the SEM. Here you can see the sample as we received it with minimal surface damage and a relatively smooth surface. The traditional swell and etch process exposes some of the glass material within the ceramic but on the whole the surface does still remain fairly smooth with additional surface debris which has failed to be removed. The sonication process however causes much more surface modification with large swathes of the glass material uncovered and no surface debris observed.



30 minutes sonication



The presence of surface debris on the traditional method is almost certainly the cause of the poor adhesion as it will form a loosely adherent interstitial layer between the surface and the electroless copper. This is not to say that this traditional process is not effective as it has been used successfully for over 20 years in the PCB industry.

4. Conclusion

Surface modification of this high Tg Epoxy can be achieved by the application of ultrasound through deionised water at 40°C. The optimal sonication time for adhesion appears to be 30 minutes. This also corresponds to highest roughness and lowest gloss readings. SEM analysis shows glass exposure but no debris. This suggests that a rough, debris free surface is important for optimal adhesion and that ultrasound does achieve surface modification at low temperatures of 40 °C in chemical free, green and environmentally friendly deionised water.

5. Acknowledgements

The authors would like to thank the IeMRC for funding this research and our industrial collaborators Chestech Ltd, Moulded Circuits Ltd and Prosonix Ltd

6. Literature

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